



Polymer-fluorinated silica composite hollow fiber membranes for the recovery of biogas dissolved in anaerobic effluent



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ABSTRACT

In this study, polymer-fluorinated silica composite hollow fiber membranes were fabricated and applied to a membrane contactor system for the recovery of methane dissolved in the anaerobic effluent. Such composite membranes allowed us to tailor the physical property such as porosity and mechanical strength and the surface hydrophobicity in separated processes. To develop the composite membranes, porous hollow fiber substrates were first fabricated with Matrimid[®], a commercial polyimide. Subsequently, fluorinated silica particles were synthesized and anchored on the substrates via a strong covalent bonding. Due to the high porosity as well as the high hydrophobicity, our membrane showed an outstanding performance for the recovery of CH₄ in the membrane contactor, such that the CH₄ flux reached 2900 mg CH₄/m²-h at the liquid velocity of 0.42 m/s at which the liquid phase still controlled the overall mass transfer. The composite membrane prepared in this work also showed a much better performance in the CH₄ recovery than a commercial polypropylene membrane made for degasification of water. In addition, a long-term test with tap water saturated with the model biogas made up of 60:40 CH₄/CO₂ mixture demonstrated that our membrane can be stably operated for more than 300 h without experiencing pore wetting problem.

1. Introduction

Anaerobic digestion is a biological process for wastewater treatment which uses microorganism to break down organic pollutants in the absence of oxygen, thereby producing biogas that contains methane, CH₄, as the major component. Since such biogas can be served as an energy source, a self-sufficient wastewater treatment process can potentially be realized if the recovery process is implemented [1]. Meanwhile, both the United States Environmental Protection Agency (EPA) and the Intergovernmental Panel on Climate Change (IPCC) have classified CH₄ as the second most prevalent greenhouse gas since it has 25 times higher global warming potential than that of CO₂ [1]. Therefore, the recovery of CH₄ from anaerobic processes can also be a solution for controlling greenhouse emission to the atmosphere.

Although biogas recovery process from the head spaces of anaerobic reactors has been well established thus far, a significant amount of CH₄ is still dissolved in the anaerobic effluents and is currently discharged without recovery processes. For example, the portion of CH₄ dissolved

in the effluent could be as high as 45% when the anaerobic reactor is operated at 30 °C and 1 atm, and this value can further increase at lower temperature [2]. In addition, to prevent any potential explosion problem, the concentration of CH₄ in the effluent must be decreased to the lower explosive limit (LEL) which is reported to be 1.4 mg/l at 15 °C and 1 bar [3]. Thus, the recovery of dissolved CH₄ can not only maximize the overall energy production capacity but also resolve the safety concern associated with potential explosion.

Multi-stage bubble column cross-flow cascades and forced draft aerators have been employed to remove dissolved CH₄ from contaminated water [4]. However, a large mass transfer unit allowing a long residence time is required to achieve 90% dissolved CH₄ removal owing to the poor mass transfer efficiency [5]. To address this issue, membrane-based technology such as membrane contactor has been proposed as a promising alternative [6]. Membrane contactor is a technology that can achieve gas/liquid or liquid/liquid mass transfer without dispersion of one phase within another. Thus, hydrophobic membranes which act as a barrier to separate gas-liquid or liquid-liquid

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streams are the key element in this technology. It can overcome the limitations of conventional contactors, such as flooding, foaming and high operating cost [7]. The absorption in which the targeted gas is transported from gas phase to liquid sorbent through membrane has been the most popular application for membrane contactor [8–12]. It can also be used in gas desorption application such as, the regeneration of chemical absorbent [13–15]. In this operation, gases physically or chemically trapped in the liquid are desorbed and transferred to the gas phase driven by partial pressure difference which is created by either sweeping gas or vacuum in the gas phase. It has been reported that hollow fiber membrane contactor can effectively perform the gas desorption at a far lower gas-to-liquid ratio than that used in the bubble column [16].

Nevertheless, a limited number of studies on the membrane-based recovery of dissolved CH₄ has been reported thus far [1]. In early studies, nonporous hollow fiber membranes have been employed in membrane contactors which were operated with vacuum [17] or sweeping gas [4] to create a driving force for CH₄ transport. However, unsatisfactory results were observed owing to the high mass transfer resistances of nonporous membranes. An improved performance was observed when microporous membrane was employed [18]. In particular, it was reported that the CH₄ recovery efficiency of microporous membrane could be 93% higher than that of nonporous membrane at a low liquid velocity. However, in the same work, a drawback of the microporous membranes was also reported as they are prone to the membrane wetting. The membrane wetting is a phenomenon in which water penetrates into membrane pores and causes an extra mass transfer resistance. It typically occurs when the surface hydrophobicity of membrane is not high enough to protect the pores from water. In addition, McLeod et al. [19] reported that the purity of CH₄ in recovered gas increased with an increase in liquid velocity or a decrease in sweeping gas flow rate. Besides, in order to get high purity CH₄, it was recommended to operate with vacuum mode. These significantly increase the transmembrane pressure and may cause the undesirable pore wetting.

All previous studies which were conducted with commercial membranes demonstrated that it is desirable for membrane to possess a high porosity together with a high hydrophobicity for this application. Such properties allow a high gas flux due to the low mass transfer resistance in membrane as well as a long term membrane stability by preventing the pore wetting problem. Herein, we report polymer-fluorinated silica composite hollow fiber membranes for the efficient recovery of CH₄ from anaerobic effluents. Two porous hollow fiber substrates possessing different structures were fabricated using Matrimid®, a commercial polyimide, to investigate the effect of morphological property on gas transport performance in membrane contactor. As the polymer doesn't have a sufficient hydrophobicity for membrane contactor application, the surfaces of membranes were then modified by depositing fluorinated silica nanoparticles that can render an excellent hydrophobicity. Subsequently, CH₄ recovery performances of the resulting membranes were evaluated and benchmarked against a commercial porous membrane. Finally, the long-term stability of membrane in a membrane contactor system was evaluated.

2. Experimental

2.1. Materials

Matrimid® 5218 was purchased from Ciba Specialty Chemicals Performance Polymers and used as the hollow fiber membrane material. *N*-methyl-2-pyrrolidone (NMP, > 99.5%, Merck), lithium chloride (LiCl, anhydrous, Merck), polyethylene glycol (PEG, MW 200, Samchun Pure Chemical), (3-aminopropyl) trimethoxysilane (APTMS, 97%, Aldrich), tetraethyl orthosilicate (TEOS, ≥ 99%, Merck), 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (PFTS, 97%, Aldrich), 2-propanol (IPA, 99.9%, Merck), ammonium hydroxide (26% NH₃·H₂O, Merck), ethanol

Table 1
Compositions of dope solutions for hollow fiber spinning.

Code	Dope composition	
MT-A	Matrimid®/LiCl/NMP	14/4/82
MT-B	Matrimid®/LiCl/PEG-200/NMP	14/2/7/77

(Merck) and *n*-hexane (96%, Merck) were used for membrane fabrication and modification. All reagents were used as received without further purifications. Purified water by a Milli-Q system (18 MΩ cm) was used as the bore fluid during the hollow fiber spinning.

2.2. Fabrication and surface modification of hollow fiber membranes

Matrimid® and LiCl were dried at 50 °C in a vacuum oven for 1 day to remove moisture prior to dope preparation. Definite amounts of the polymer, additives (PEG and LiCl) and solvent were mixed in a jacket flask equipped with an overhead stirrer and kept at 60 °C which was precisely controlled by a circulator bath. The compositions of polymer dopes (denoted as MT-A and MT-B) are shown in Table 1. After the polymer is completely dissolved, the dope solution was cooled down to room temperature and subsequently degassed under a mild vacuum overnight prior to spinning. Next, porous hollow fiber substrates were fabricated by the dry-jet wet spinning process using conditions listed in Table 2. In the spinning process, the dope was extruded through a spinneret at a controlled rate and went through a certain air gap before immersing into the coagulation bath. The hollow fibers fabricated were then stored in a water bath for at least 2 days to completely remove residual solvent and additives. Finally, the membranes were immersed in glycerol/water (1:1) mixture to prevent shrinkage during the following drying process at room temperature.

To render a hydrophobicity to both MT-A and MT-B substrates, fluorinated silica nanoparticles were formed and anchored on the polyimide membrane surfaces via covalent bonding formed by cyclic imide ring opening reaction. The detailed procedure is described elsewhere [20]. Briefly, the imide group of Matrimid® membrane was reacted with the amino group of APTMS to form amide group in the first step. Subsequently, the APTMS-treated Matrimid® membrane was immersed in the SiO₂ precursor (TEOS) solution in which APTMS bound to the membrane surfaces reacted with TEOS to form SiO₂ nanoparticles. Finally, the membrane with SiO₂ nanoparticles were soaked in a PFTS solution, such that the PFTS molecules were apt to react with the silanol groups on SiO₂ particles. Depending on the substrates, the surface modified membranes were denoted as Mo-MT-A and Mo-MT-B, respectively

2.3. Membrane characterizations

The dimensions of hollow fiber membranes were examined using a digital microscope (KEYENCE, VHX-500F). The cross section and the surface morphologies of membranes were observed with Scanning Electron Microscope (SEM, JSM-7200F JOEL) at an operation voltage of 5 kV. Dried membrane samples were cryogenically fractured in liquid

Table 2
Hollow fiber spinning conditions.

Parameter	Value
Bore fluid (NMP/H ₂ O) (wt%)	80/20
Bore fluid flow rate (ml/min)	2
Air gap (cm)	5
Take up speed	Free fall
External coagulant	Tap water
Spinning temperature (°C)	25
Spinneret diameter (OD/ID) (mm)	1.5/0.7

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